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LOUIS D. QUIN

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The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

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FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

7-Phosphanorbornenes, Metaphosphates, Metaphosphoramidates,
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Oxaphosphabicyclo[2.2.2]octenes, 2-Phosphabicyclo[2.2.2]-

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Numerous derivatives of metaphosphoric acid were generated by thermolysis of 2,3-oxaphosphabicyclo[2.2.2]octene derivatives, through an apparent retrocycloaddition process. Metaphosphonic acid anhydrides were similarly generated. These low-coordination species are recognized by trapping reactions with alcohols, amines, epoxides, and in certain cases with N-methylpyrrole and silica gel. The latter is converted to a novel phosphorylated form having potential practical applications. Phosphaalkenes were also generated by thermolysis of derivatives with the 7-phosphabicyclo[2.2.2] octadiene ring system, and recognized by trapping reactions with dienes.

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Louis D. Quin

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octadienes, Phosphorylated Silica Gel, Phosphaalkenes.

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GENERATION OF PHOSPHORUS ESTER, PHOSPHORUS AMIDE, AND PHOSPHINE
DERIVATIVES OF LOW COORDINATION NUMBER

FINAL REPORT

LOUIS D. QUIN

DECEMBER 10, 1989

U.S. ARMY RESEARCH OFFICE
POST OFFICE BOX 12211
RESEARCH TRIANGLE PARK, NC 27709

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UNIVERSITY OF MASSACHUSETTS
AMHERST, MA 01003

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REPORT OF INVENTIONS AND SUBCONTRACTS

(Pursuant to "Patent Rights" Contract Clause) (See Instructions on Reverse Side.)

Form Approved
OMB No. 0704-0240
Expires Feb 28, 1987

1a. NAME OF CONTRACTOR / SUBCONTRACTOR Louis D. Quin	c. CONTRACT NUMBER DAAL03-86-K-0159	2a. NAME OF GOVERNMENT PRIME CONTRACTOR	c. CONTRACT NUMBER	3. TYPE OF REPORT (X one) a. INTERIM <input checked="" type="checkbox"/> b. FINAL <input type="checkbox"/>
b. ADDRESS (Include ZIP Code) Univ. of Massachusetts Amherst, MA 01003	d. AWARD DATE (YYMMDD) 1 July 1986	b. ADDRESS (Include ZIP Code)	d. AWARD DATE (YYMMDD)	4. REPORTING PERIOD (YYMMDD) a. FROM 1 July 1986 b. TO 14 October 1989

SECTION I - SUBJECT INVENTIONS

5. "SUBJECT INVENTIONS" REQUIRED TO BE REPORTED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)		6. EMPLOYER OF INVENTOR(S) NOT EMPLOYED BY CONTRACTOR/SUBCONTRACTOR		7. ELECTED FOREIGN COUNTRIES IN WHICH A PATENT APPLICATION WILL BE FILED		8. CONFIRMATORY INSTRUMENT OR ASSIGNMENT FORWARDED TO CONTRACTING OFFICER	
a. NAME(S) OF INVENTOR(S) (Last, First, Middle Initial)	b. TITLE OF INVENTION(S)	(1) (a) Name of Inventor (Last, First, Middle Initial)	(b) Name of Employer	(1) United States (a) Yes <input type="checkbox"/> No <input type="checkbox"/>	(2) Foreign (b) Yes <input type="checkbox"/> No <input type="checkbox"/>	(1) Yes <input type="checkbox"/> No <input type="checkbox"/>	(2) No <input type="checkbox"/>
None							

SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

6. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)		7. SUBCONTRACTS AWARDED BY CONTRACTOR/SUBCONTRACTOR (If "None," so state)		8. SUBCONTRACT DATES (YYMMDD)	
a. NAME OF SUBCONTRACTOR(S)	b. ADDRESS (Include ZIP Code)	c. SUBCONTRACT NO.(S)	d. "PATENT RIGHTS" (1) Clause Number (2) Date (YYMM)	e. DESCRIPTION OF WORK TO BE PERFORMED UNDER SUBCONTRACT(S)	(1) Award (2) Estimated Completion

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7. CONTRACTOR / SUBCONTRACTOR Louis D. Quin		8. CONTRACTOR / SUBCONTRACTOR Univ. of Massachusetts		9. CONTRACTOR / SUBCONTRACTOR Amherst, MA 01003	
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	Principal Investigator	Louis D. Quin	Grant & Contract Admin.		

INSTRUCTIONS

GENERAL

This form is for use in submitting INTERIM and FINAL invention reports to the Contracting Officer and for use in the prompt notification of the award of subcontracts containing a "Patent Rights" clause. If the form does not afford sufficient space, multiple forms may be used or plain sheets of paper with proper identification of information by Item No. may be attached.

An INTERIM report is due at least every 12 months from the date of contract award and shall include (a) a listing of "Subject Inventions" during the reporting period, (b) a certification of compliance with required invention identification and disclosure procedures together with a certification of reporting of all "Subject Inventions," and (c) any required information not previously reported on subcontracts awarded during the reporting period and containing a "Patent Rights" clause.

A FINAL report is due within 6 months if contractor is a small business firm or domestic nonprofit organization and within 3 months for all others after completion of the contract work and shall include (a) a listing of all "Subject Inventions" required by the contract to be reported, and (b) any required information not previously reported on subcontracts awarded during the course of or under the contract and containing a "Patent Rights" clause.

While the form may be used for simultaneously reporting inventions and subcontracts, it may also be used for reporting, promptly after award, subcontracts containing a "Patent Rights" clause.

Dates shall be entered where indicated in certain items on this form and shall be entered in four or six digit numbers in the order of year and month (YYMM) or year, month and day (YYMMDD). Example: April 1986 should be entered as 8604 and April 15, 1986 should be entered as 860415.

Item 1a. Self-explanatory.

Item 1b. Self-explanatory.

Item 1c. If "same" as item 2c, so state.

Item 1d. Self-explanatory.

Item 2a. If "same" as item 1a, so state.

Item 2b. Self-explanatory.

Item 2c. Procurement Instrument Identification (PII) number of contract (DFAR 4.7003).

Item 2d thru 5e. Self-explanatory.

Item 5f. The name and address of the employer of each inventor not employed by the contractor or subcontractor is needed because the Government's rights in a reported invention may not be determined solely by the terms of the "Patent Rights" clause in the contract.

Example 1: If an invention is made by a Government employee assigned to work with a contractor, the Government rights in such an invention will be determined under Executive Order 10096.

Example 2: If an invention is made under a contract by joint inventors and one of the inventors is a Government employee, the Government's rights in such an inventor's interest in the invention will also be determined under Executive Order 10096, except where the contractor is a small business or nonprofit organization, in which case the provisions of Section 202 (e) of P.L. 96-517 will apply.

Item 5g (1). Self-explanatory.

Item 5g (2). Self-explanatory with the exception that the contractor or subcontractor shall indicate, if known at the time of this report, whether applications will be filed under either the Patent Cooperation Treaty (PCT) or the European Patent Convention (EPC). If such is known, the letters PCT or EPC shall be entered after each listed country.

Item 6a. Self-explanatory.

Item 6b. Self-explanatory.

Item 6c. Self-explanatory.

Item 6d. Patents Rights Clauses are located in FAR 52.227

Item 6e thru 7b. Self-explanatory.

Item 7c. Certification not required by small business firms and domestic nonprofit organizations.

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I. PURPOSE OF THE RESEARCH PROGRAM

The 7-phosphanorbornene system is synthetically readily approached, and because of the considerable strain involved in the bridged structure, a mechanism exists for the novel insertion reaction of oxygen into a C-P bond. This creates another ring system (1,2-oxaphosphabicyclo[2.2.2]octene) potentially capable of undergoing a retro[4+2] cycloaddition to release a phosphoryl compound ($R-PO_2$) of low coordination. A related part of the program involves the synthesis and fragmentation of the phosphabicyclo[2.2.2]octene system which should provide phosphalkenes ($RP=CH_2$). This report summarizes work both on the precursor syntheses, as well as on the successful generation of several low-coordination species. The original concept behind the project has been amply demonstrated experimentally.

II. MAJOR ACCOMPLISHMENTS

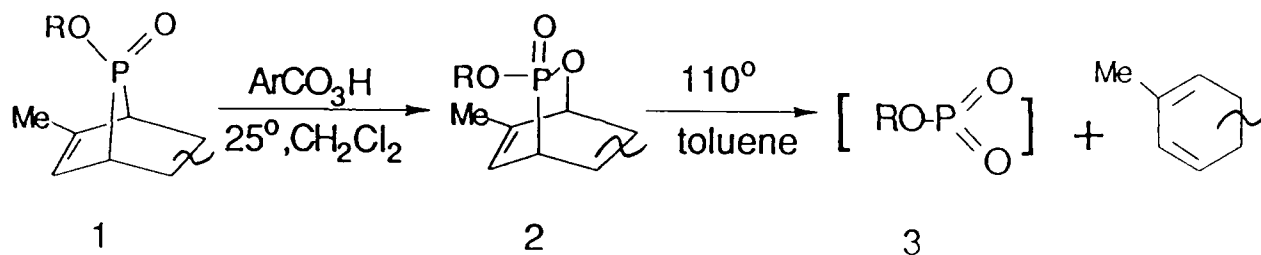
1. Introduction

This project was first started as Grant DAAL03-86-K-0028 on December 15, 1985, for a three-year period while the Principal Investigator was at Duke University. In July, 1986, the PI transferred to the University of Massachusetts, and the grant was assigned a new number (DAAL03-86-K-0159) for the period August 15, 1986 - December 14, 1988. A no-cost extension was then granted to October 14, 1989. This report reviews the major accomplishments for the entire period of December 15, 1985 - October 14, 1989. Most of the work has been published and only important conclusions will be presented here. Disruption of the project due to the move of the laboratory was minor and progress has been considerable.

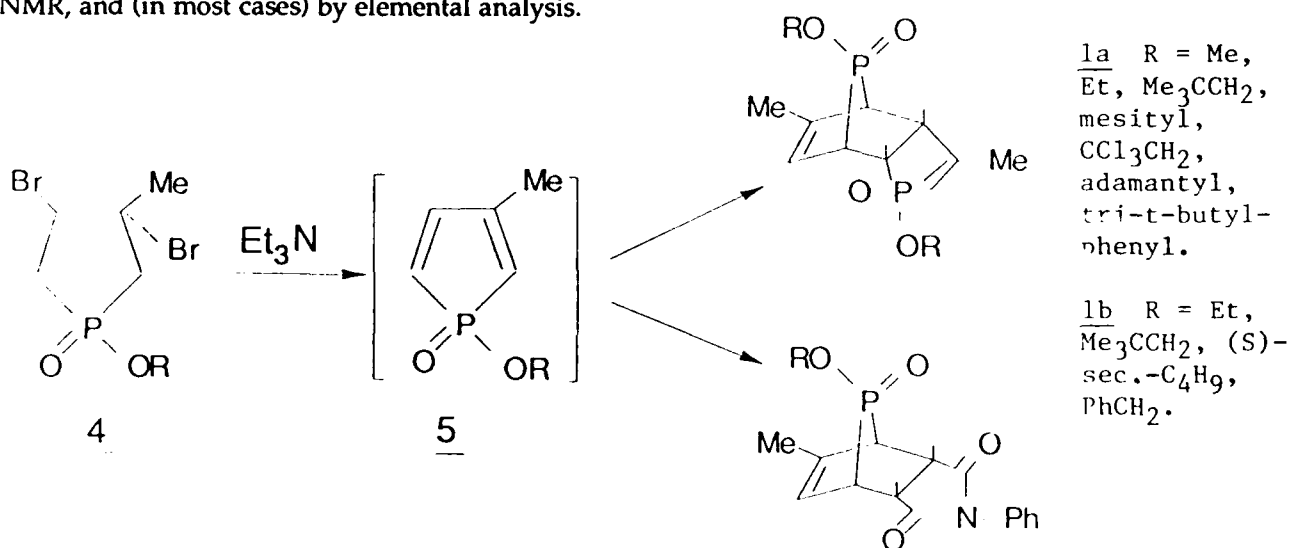
The major objective of the project is to develop a new synthetic approach to low-coordination phosphorus species and to consider practical applications for these highly reactive species. Emphasis has been given to the family of metaphosphoric acid ($HO-PO_2$) derivatives and to phosphalkenes ($RP=CH_2$); some exploratory work on the species $Ar-PO_2$ has also been performed.

2. Generation and Trapping of Some New Metaphosphates

In earlier work,¹ it was shown that the reactions below constituted a useful new way to generate the ethyl ester (3) of metaphosphoric acid.

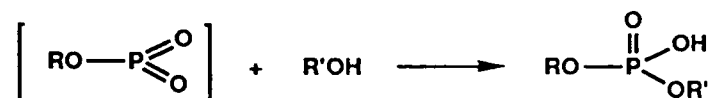


Metaphosphates are highly reactive in solution, and are only detectable from reaction with trapping agents. In this project, alcohols or N-methylpyrrole are used as trapping agents, the former giving phosphate esters, the latter giving the 2-phosphonate. This new process has now been shown to have great generality. A variety of metaphosphates have been generated by employing different alcohols in the synthesis of the precursors (4) to the phosphole oxides (5) used to create the bridged structures (1) shown above. During the project period, the bridged structures 1a and 1b were prepared by dimerization or Diels-Alder reaction with N-phenylmaleimide. Considerable effort was expended in developing the synthetic procedures, and all products and intermediates were characterized by ^1H , ^{31}P , and ^{13}C NMR, and (in most cases) by elemental analysis.

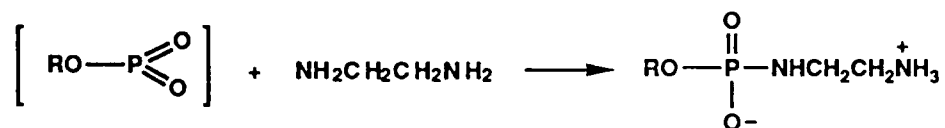


The critical O-insertion reaction was successfully performed on all of the bridged structures, except for 1a, R = 2,4,6-tri-*t*-butylphenyl, which was so badly hindered that it reacted at an impractically slow rate with *m*-chloroperbenzoic acid. The adamantyl derivative of 1a was also severely hindered, but gave a satisfactory result after a prolonged reaction period (three weeks). Again all products have been fully characterized.

From most of the bicyclic phosphonates 2 prepared from 1a, metaphosphates were successfully generated by thermolysis (110°) in toluene solution. In each case, the metaphosphate was trapped with an alcohol, and the resulting phosphate isolated by chromatography and characterized spectrally. A variety of alcohols have been used for this purpose, including ethyl, *n*-propyl, *n*-heptyl, *t*-butyl, and cyclohexyl.



Amines are also useful trapping agents, and one of special interest, because of the novelty of the structure, is ethylenediamine.



Such phosphoramidates are difficult to generate by other methods.

3. Mechanistic Considerations.

Detailed studies of the mechanism of the thermolysis process have recently been initiated. While this phase of our work is not complete, we have accumulated kinetic evidence that supports a unimolecular, retrocycloaddition process where the alkyl metaphosphate is released as a discrete but very short-lived, intermediate. Thus, the reaction of 1b, R = Et is first-order in CHCl₃ or DMSO over the temperature range 70-100°; the rate is not affected by the addition of a several-fold excess of ethanol as a trapping agent, excluding the possibility of a reaction directly between the trapping agent and precursor. The rate constants at 100° are in the ratio ¹k(DMSO)/¹k(CHCl₃) = 12 which indicate

very little solvent stabilization of a transition state by the highly polar DMSO, and points to a concerted, rather than 2-step ionic mechanism. The entropy of activation is relatively small (-12 to -14 cal/deg), consistent with other [4+2] retrocycloaddition processes.

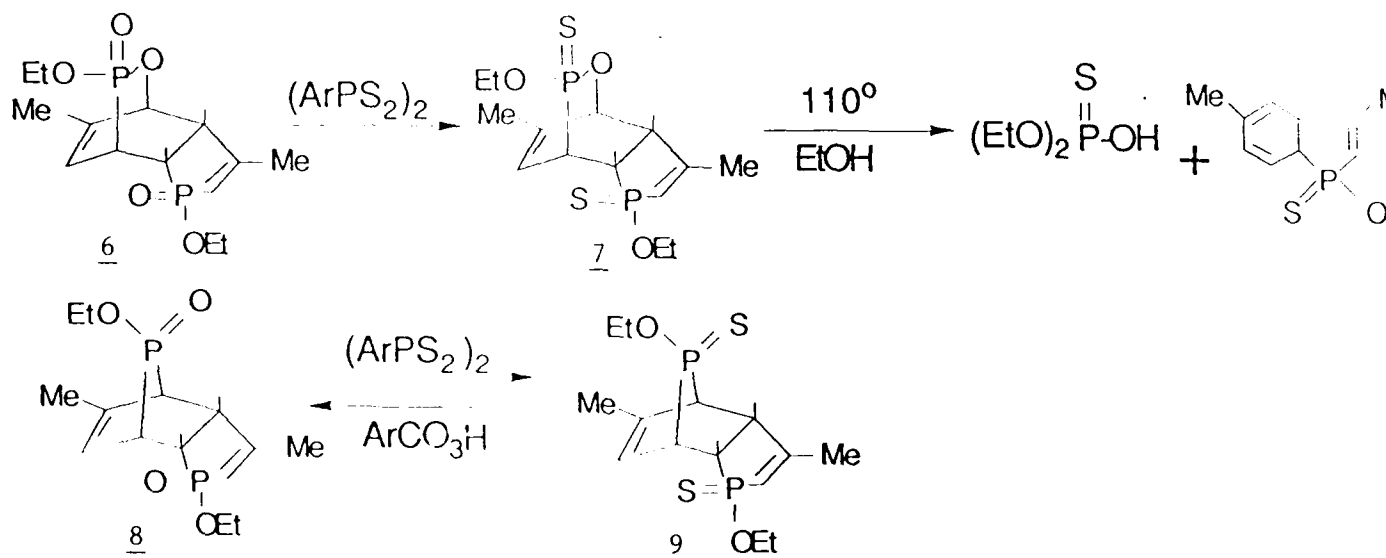
Another approach to confirming the intermediacy of a metaphosphate as a real species involves stereochemical concepts with thio derivatives, and is presented in section 4.

The reason large groups like neopentyl, adamantyl, and mesityl were incorporated in the metaphosphate precursor is to provide kinetic stabilization of the product. This is an approach which has had considerable success in the stabilization of a variety of low-coordination species. In the present case, however, the large group is one atom removed from P, and the effect may not be so large as to give adequate stabilization. Of the metaphosphate precursors (2) prepared so far, that with adamantyl on oxygen has the best chance of giving a stabilized product. Experiments to fragment this bridged phosphonate in such a way as to probe for the presence of the metaphosphate were not successful, however. The decomposition takes a different pathway, which appears to involve a retrocycloaddition with elimination of a phosphole oxide molecule. With the availability of a precursor for neopentyl metaphosphate, we are now in a position to study the thermal fragmentation in the probe of an NMR spectrometer where we may be able to observe the intermediate before polymerization. Another approach will be to employ a photochemical generation method we have developed in a separate but related project,² since this can be performed at low temperatures.

4. Generation of Alkyl Metathiophosphates.

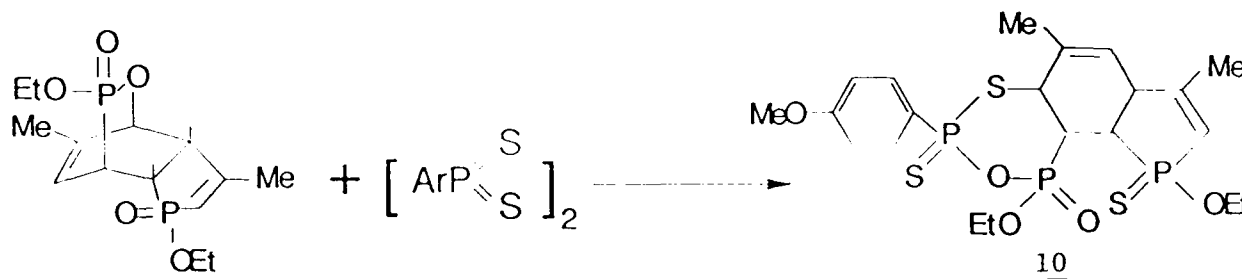
We have had great success in synthesizing precursors that would lead to the presently unknown family of alkyl thiometaphosphates, RO-P(S)O on fragmentation. Our approach has been to replace the phosphoryl oxygen in the bridged phosphonates of type 1a or 1b by sulfur, using for this purpose the reagents P₂S₅ or (ArPS₂)₂ (Lawesson's reagent). The products would be precursors on thermolysis of the thiometaphosphates. The anion of the corresponding acid has recently been generated,³ and is of interest since it seems to have longer lifetime than the oxygen analogue. Our first approach involved the conversion of P=O to P=S in the bridged phosphonate 8 with Lawesson's reagent at 25°, a process

which gave a complicated mixture nevertheless possessing ^{31}P NMR signals in the expected region for the dithiono compound 7. Thionation causes downfield shifts, and the product contained strong doublets ($J = 75.6 \text{ Hz}$) at +89.3 and +114.5. These signals constituted about 50% of the product. Repeated attempts at chromatographic purification increased the purity only to about 70%. The same product was approached by first performing the thionation on the phosphole oxide dimer 8, followed by oxygen insertion with a peracid. The thionation gave a crystalline product 9 in good yield, but in the peracid oxidation step, reaction occurred first on sulfur in this compound, without giving the desired O-insertion, and the original oxide was regenerated. The crude sample of 7 was therefore used in a thermolysis at 110° in toluene with ethanol as trap, and a new product appeared with a ^{31}P NMR signal in the expected location for the trapped product, $(\text{EtO})_2\text{P}(\text{S})\text{OH}$. The value was +63.5; a reported value is +64.⁴ This product was extracted from the mixture with aqueous base. Only one other compound, with ^{31}P +81, was co-extracted; it has not yet been identified. This mixture was studied by mass spectrometry, which confirmed the presence of the thiophosphate by giving a strong signal with m/z correct for M^+ (170).

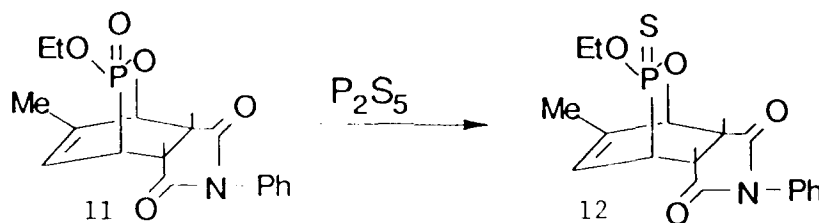


When the thionation of the bridged phosphonate 6 was attempted at 110° with Lawesson's reagent, the reaction mixture was dominated by a different product. This material is formed also at room temperature but in smaller amounts. It proved to be readily isolated by silica gel chromatography.

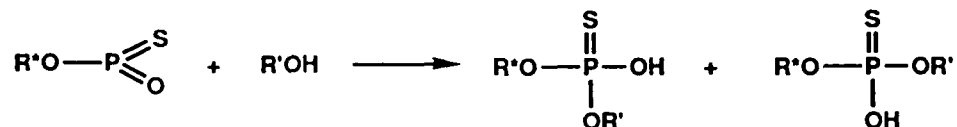
This material, a crystalline solid of mp 159-161°, had three ^{31}P NMR signals: δ +18.9 (d of d, $J=37.9$, 5.8 Hz), δ +86.6 (d, $J=37.9$), δ +118.5 (d, $J=5.8$). The molecular formula from mass spectral analysis was $\text{C}_{21}\text{H}_{29}\text{O}_5\text{P}_3\text{S}_3$. This corresponds to addition of the monomeric form of Lawesson's reagent, itself a low-coordination species, to a ring-opened, mono-thionated version of the starting bridged phosphonate. The novel structure 10 was determined by X-ray crystallographic analysis.



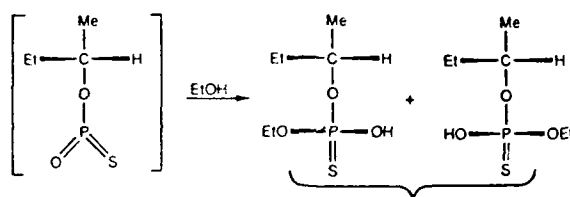
In more recent work, it has been found that the Diels-Alder adduct 11 is greatly to be preferred as the bridged phosphonate used in the thionation reaction. The reaction products from either P_2S_5 or Lawesson's reagent were quite clean, with the product accounting for 90-95% of the mixture. The ^{31}P NMR signal was found at +86.1, as expected for 12. This material has been purified and is a crystalline solid with mp 138-139° that gives the correct elemental analysis. The thiometaphosphate was generated in the presence of ethanol, and the only P-containing product was the desired $(\text{EtO})_2\text{P}(\text{S})\text{OH}$. It is clear that this is a simple, efficient way to generate the new family of thiometaphosphates, and the process is being extended to provide other derivatives. One of particular importance is stabilized with the bulky neopentyl group; the bridged thionophosphonate has been successfully prepared and gives the metathiophosphate on heating as determined from trapping reactions. Attempts to observe the metathiophosphate directly by NMR will soon be made.



As noted in Section 3, alkyl metathiosphosphates have been employed in studies to establish the existence of such species as real intermediates. Metaphosphates should have planarity at phosphorus, and attack by a nucleophile should proceed at the same (or nearly the same) rate from either face. When S replaces O, diastereomeric products are possible with an optically active substituent and presumably are observable by ^{31}P NMR.



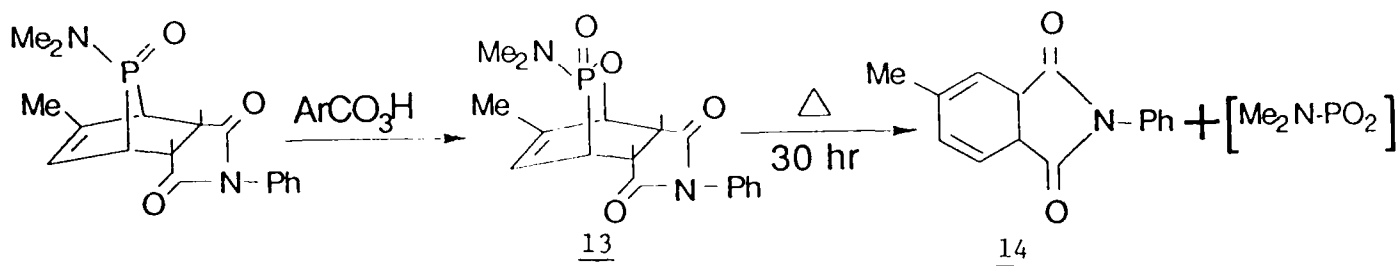
We have shown that this is in fact the case by synthesizing an optically active metathiosphosphate and observing the composition of the ethanol trapping product. This proved to have the nearly 1:1 ratio of diastereoisomers predicted for a planar species.



The same result was obtained when $\text{EtO}-\text{P}(\text{S})\text{O}$ was reacted with (S)-sec. butyl alcohol, and we feel these reactions provide strong evidence for a finite lifetime for the planar metathiosphosphate.

5. Generation of N,N-Dimethylaminometaphosphate.

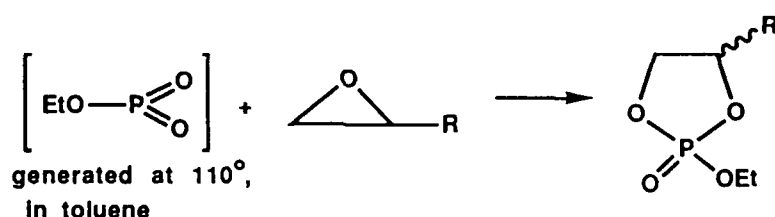
Another species generated and trapped during this program has the structure $\text{Me}_2\text{N}-\text{PO}_2$. It has been approached by the same general method, namely, the thermal fragmentation of a bridged phosphonamidate. The results of this study have been published in detail⁵ and will not be repeated here. The major accomplishments were the synthesis of the new bridged phosphonamidate **13** by the O-insertion method, its stereochemical assignment by NMR and by X-ray diffraction analysis, and the thermal fragmentation of this compound to provide products expected from the desired elimination of the P-O bridge.



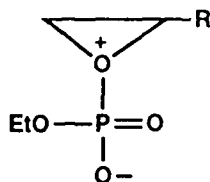
Compared to the reaction under the same conditions in toluene of the corresponding ethyl ester, the rate of this fragmentation was markedly slower. The dihydrophthalimide 14 was isolated from the thermolysis mixture and identified spectrally. The species Me_2NPO_2 proceeded to react with itself and gave the usual P-O-P derivatives with ^{31}P NMR shifts in the 0 to -20 range. It was found that primary alcohols function as trapping agents for $\text{Me}_2\text{N-PO}_2$, and cleanly gave dialkyl phosphates as dimethylamine salts. Apparently, alcoholysis of the initial trapping product $\text{Me}_2\text{NP(O)(OEt)OH}$ occurred during the process. In work on another project,² the same bridged phosphonamide 13 was found to be easily fragmented photochemically at 35° ; this is a more attractive way to generate metaphosphoramidates since the secondary reaction of the trapping agent can be avoided, and is being further examined.

6. New Reactions of Metaphosphates.

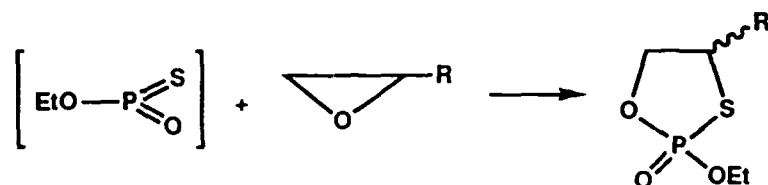
(a) *With Epoxides.* We have carried out several exploratory reactions to expand the knowledge of the reactivity of metaphosphate species. One new reaction that works well is that with epoxides, which gives 1,3,2-dioxaphospholane 2-oxide derivatives.



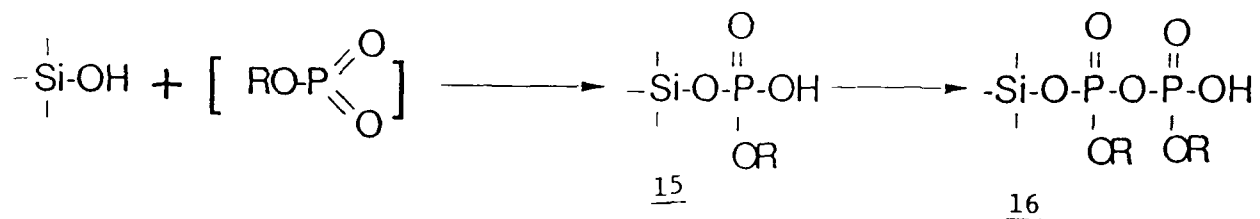
The reaction is presumed to start with electrophilic attack on the epoxides. Further aspects of the mechanism for formation of the cyclic product are now being examined.



Alkyl metathiophosphates react similarly to form the 1,3,2-oxathiaphospholane ring.



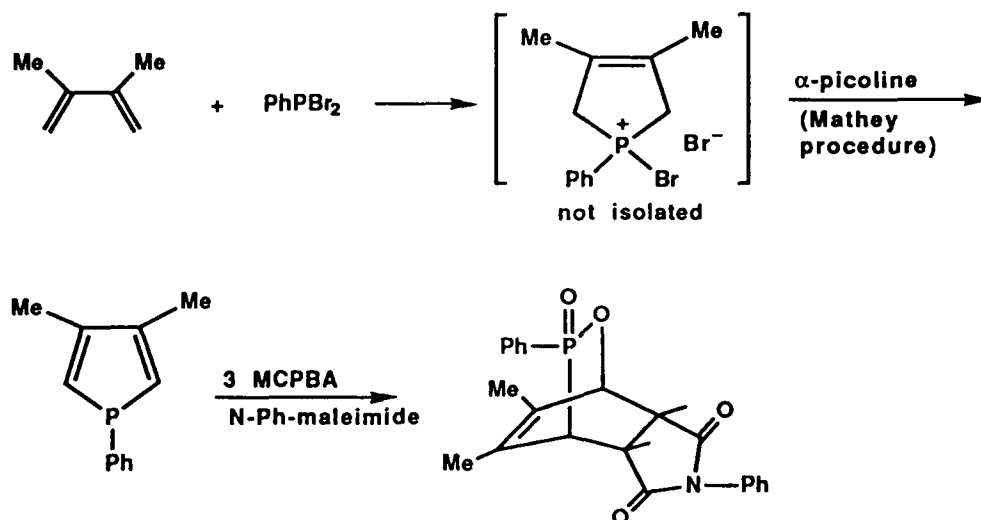
(b) *With Silica Gel.* It is well known that the OH groups on the surface of silica gel are reactive to strongly electrophilic species. We have found that silica gel, when present in the medium of generation of a metaphosphate, is easily phosphorylated. This discovery forms the basis for much new work under a new grant from ARO. The preliminary experiments that have been completed have been published.⁶ The basic process is represented below.



The initially-formed 15 is itself reactive to ethyl metaphosphate, giving a pyrophosphate 16, as revealed by performing CP-MAS ³¹P NMR spectroscopy on the solid. In more recent work, we have been able to stop the reaction at the stage of 15. The discovery of the reactivity of silica gel to a metaphosphate opens up many paths for research; various groups may be placed directly on the surface of silica gel to endow it with special properties, and other OH-bearing solids may be reactive under similar conditions. The materials produced could have valuable properties as adsorbents or as catalysts.

7. Generation of the Species Ph-PO₂.

We have devised a two-step process that proceeds in excellent yields for the preparation of a generator for Ph-PO₂, the meta-anhydride of a phosphonic acid.



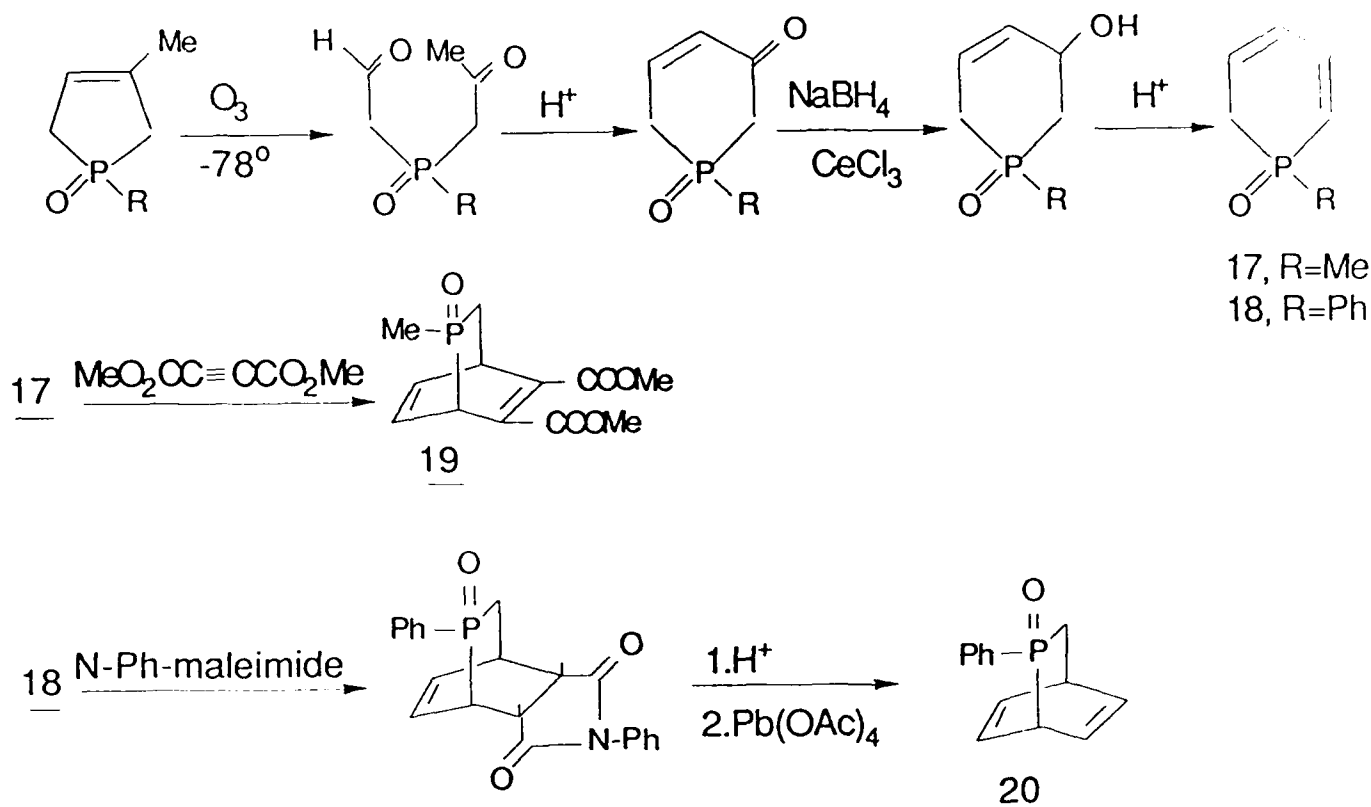
Three events occur in the one pot used for the MCPBA reaction: oxidation of the phosphole to the phosphole oxide, Diels-Alder reaction of this oxide with N-phenylmaleimide, O-insertion into the C-P bond. The fragment Ph-PO₂ has been generated thermally (110° in toluene) and photochemically (30°, 254 nm, dioxane) in excellent yields. With this improved access to this highly reactive species, its chemistry can be studied with ease. It is hoped soon to perform a fragmentation at -78° by the photochemical method.

8. Generation of Phosphaalkenes by Fragmentation of 2-Phosphabicyclo[2.2.2]octadienes.

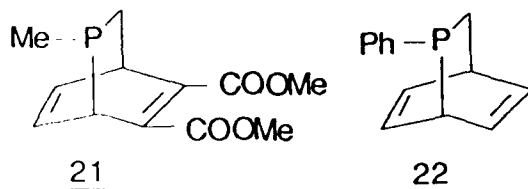
The synthesis of the bridged phosphine oxides 19 and 20 has been accomplished and the results published.⁷ The major steps in these syntheses are shown in Scheme 1.

We have now devised reproducible procedures that allow the removal of the oxygen from phosphorus, providing the corresponding phosphines 21 and 22. Special conditions are necessary to prevent premature fragmentation of these delicate materials; usually, such deoxygenations are conducted in refluxing benzene, but this procedure gave no useful results. We have found that the

Scheme 1

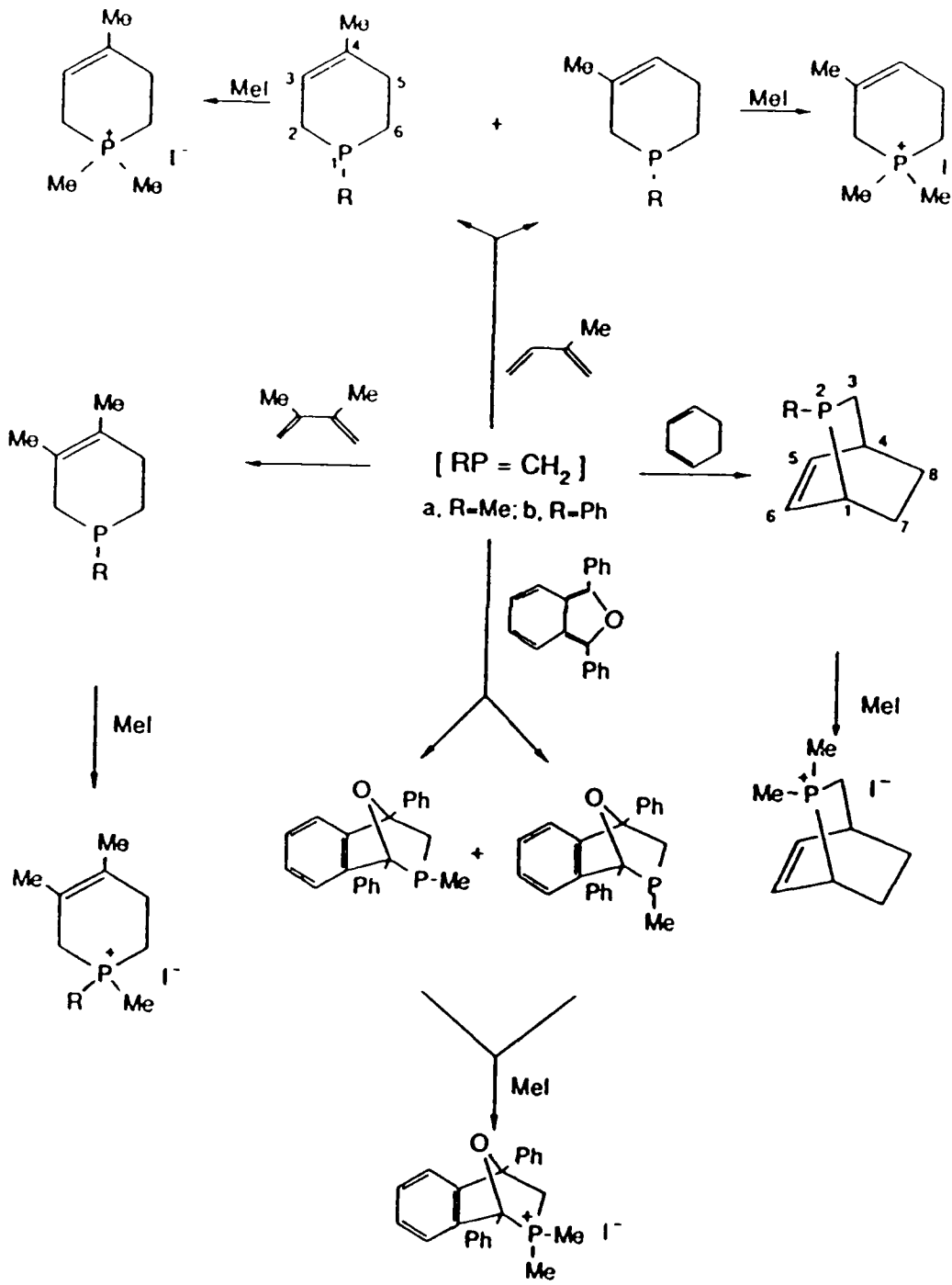


deoxygenation occurs under very mild conditions (0-25°), with methylene chloride as the solvent. Phosphines 21 and 22 have been fully characterized spectrally, including the use of two-dimensional NMR. Phosphine 21 has been analyzed as the methiodide. Complete details on the synthesis and characterization are included in a recent⁷ paper. Phosphine 21 was found to decompose at 40° in about 5 hours,



giving dimethyl phthalate and derivatives from the ejected fragment $R-P=CH_2$. The P-phenyl phosphine 22 decomposed at even lower temperatures (30°C) to give similar products. We have now successfully trapped these new phosphathenes, before they react with themselves, by including dienes in the decomposition medium. A Diels-Alder reaction occurs to give a six-membered cycloaddition product. Some of the structures formed in the trapping reactions are shown in Scheme 2.

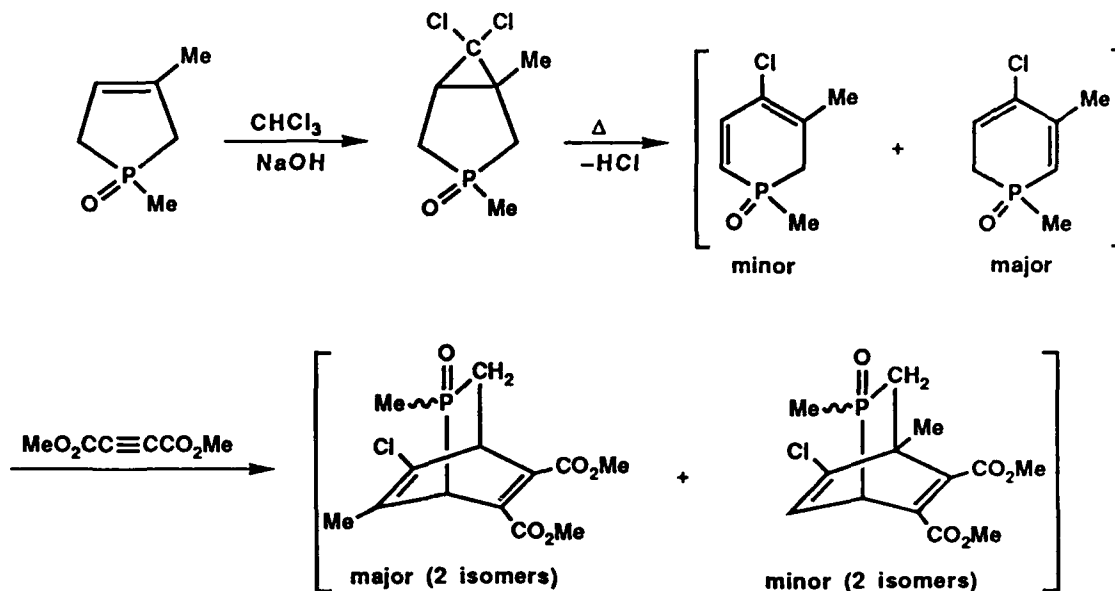
SCHEME 2



These new compounds have been fully characterized, and are reported in a paper that has been published.⁸

This fragmentation method represents a new approach to phosphalkenes, and can be extended to prepare other compounds. It offers an advantage in leading to phosphathenes with no substituents on the methylene group. Usually, large substituents are placed there to stabilize the species. We have purposely avoided stabilized species so that the reactivity of the phosphalkenes will not be impeded and can be readily observed and exploited.

A difficulty with our procedure is the length of the synthetic method needed to generate the immediate precursor. We are now exploring a new and simpler approach, which starts also with a 3-phospholene oxide but provides the precursor in four rather than seven steps. Here the dihydrophosphinine intermediate is generated by use of a published procedure⁹ involving dichlorocarbene addition to the phospholene double bond, and the thermal rearrangement with HCl elimination. We have shown that the Diels-Alder step works well and that the desired bicyclo[2.2.2]octadiene is formed as a mixture of two regioisomers, each as two diastereoisomers. Separation by chromatography is feasible, and we are now exploring the HSiCl_3 reduction to provide the phosphine. Preliminary results were successful and established that the new phosphines did fragment to the species $\text{MeP}=\text{CH}_2$. Work is continuing to develop this new synthetic approach.



9. ^{17}O NMR of Phosphoryl Compounds.

As a result of some of the synthetic work on this project, as well as in other work, a number of phosphoryl compounds with various heterocyclic frameworks have become available. We have proceeded to determine the natural abundance ^{17}O NMR spectra of these compounds, since very little is known about this potentially valuable parameter. We were surprised to find that the range of shifts can be very large, nearly 100 ppm, and of value in structural analysis. The results have been published.¹⁰ We also found¹¹ that a good correlation existed between the ^{17}O shifts of the phosphine oxides and the ^{31}P NMR shifts of the corresponding phosphines (and not the phosphine oxides). The correlation is linear. Phosphines with the 7-phosphanorbornene structure have the most downfield ^{31}P NMR shifts known, and the corresponding oxides have the most downfield ^{17}O shifts known. Also, rings with three members are at the extreme of shielding for both parameters. Various other ring systems fit nicely between these extremes. It is not yet understood why the correlation should exist, but it may prove valuable in an empirical way, as well as being of theoretical interest.

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III. PUBLICATIONS RESULTING FROM THIS GRANT

A. Published Papers

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1. Louis D. Quin, Principal Investigator, 1 July 1986 - 14 October 1989
2. Fayez H. Osman, Postdoctoral Research Associate, 1 August 1986 - 30 September 1987
3. Narayan D. Sadanani, Postdoctoral Research Associate, 13 October 1987 - 14 October 1989
4. Ryszard Bodalski, Visiting Associate Professor, 8 January 1989 - 14 October 1989
5. Gyongyi S. Quin, Postdoctoral Research Associate, 1 September 1989 - 14 October 1989
6. Xiao-Ping Wu, Predoctoral Research Assistant, 1 July 1986 - 14 October 1989
7. Li-Qiu Wang, Departmental Assistant, 19 July 1987 - 10 June 1989
8. Jian-Sheng Tang, Research Fellow, 16 July 1989 - 14 October 1989